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Discontinuous Enhancement of Crystal Growth below Glass Transition

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結晶成長速度はガラス転移温度に近づくにつれて結晶化速度は急激に遅くなり、通常はガラス転移温度（T_g）以下では結晶化が進行しないと考えられている。しかし、T_g を境に結晶化が不連続に促進されるという不思議な現象が幾つかの物質について報告されている。この原因について、我々はガラスから結晶へ凝集した際、その界面に過剰な自由体積が与えられるために、その周りのガラスが液体状態として振舞ったと考え、このモデルの妥当性を実験により確かめた。

The growth rate G of crystal can be described in terms of the difference in the free-energy between liquid and crystal, ΔF, and the translational diffusion constant, D, as $G \propto \Delta FD$ [1]. Thus, G becomes extremely small when T is either near melting temperature T_m or near glass transition temperature T_g. Contrary to this common sense, Oguni and coworkers found discontinuous enhancement of crystal growth (DECG) behavior just below T_g for some molecular liquids [2] by observing the growth of a crystal from the surface of a crystal previously formed above T_g. The increase of the growth rate across T_g is far more than one order of magnitude. They explained this phenomenon by their homogeneous nucleation based (HNB) crystallization scenario. It was also suggested that this phenomenon occurs only in molecules having phenyl rings [2]. However, why the growth rate is suddenly accelerated by many orders of magnitude across T_g and what are the roles of phenyl rings remain open questions.

To explain this phenomenon, one of us (H.T) proposed that the volume contraction on crystallization provides the free volume to molecules surrounding a crystal, increases their mobility, and accelerate the crystal growth [3]. Here we aim at experimentally checking the validity of this scenario using *o*-terphenyl (OTP), phenyl salicylate (salol), which has two crystalline forms, and indomethacin especially from a view point of the specific volume V and temperature dependence.

The DECG behavior were confirmed for OTP and form I and II of salol. Figures 1(a) and (b) show the temperature dependence of G, respectively, for OTP and salol (form I and II). G discontinuously increases by a factor of 10^2-10^4 across T_g with a decrease in the crystallization temperature T_x. For salol the degree of the enhancement is smaller for form II than for form I.

The values of ΔV for OTP (0.042 cm^3/g)[4] and form I of salol (0.045 cm^3/g) [5] are similar, whereas the value of ΔV for form II (0.037 cm^3/g) [5] is smaller than that of form I. Our finding

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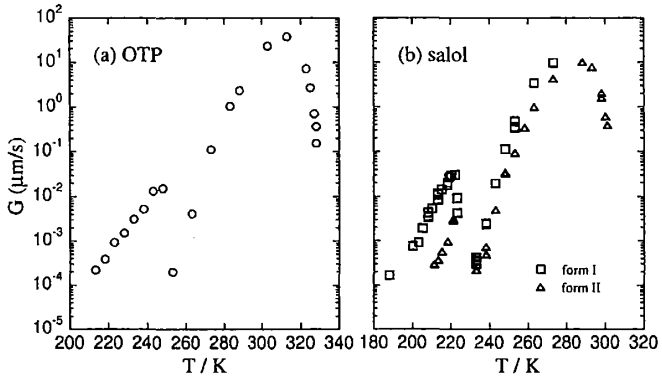

Figure 1: Temperature dependence of G for (a) OTP and (b) salol. In (b) squares are for form I of salol, and triangles for form II.

that G of form I of salol below T_g is larger than that of form II is consistent with this difference in ΔV according to our scenario, where the larger volume contraction (larger ΔV) should provide the larger excess free volume and thus lead to the larger enhancement of mobility at the growth interface.

Indomethacin has phenyl rings in the chemical structure, but it does not exhibit the DECG behavior. Thus the presence of phenyl rings cannot be used as a criterion. The value of ΔV of indomethacin (0.032 cm^3/g) [6] is smaller than those of OTP and form I and II of salol. So we believe that the criterion for the occurrence of the DECG behavior is that $\Delta V > \Delta V_c$. The existence of phenyl rings in a molecular structure may be positively correlated with ΔV.

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